Monitored Natural Attenuation Ten Years After: Technology Status

U.S. Army Corps of Engineers
Huntsville Engineering & Support Center
Environmental & Munitions CX

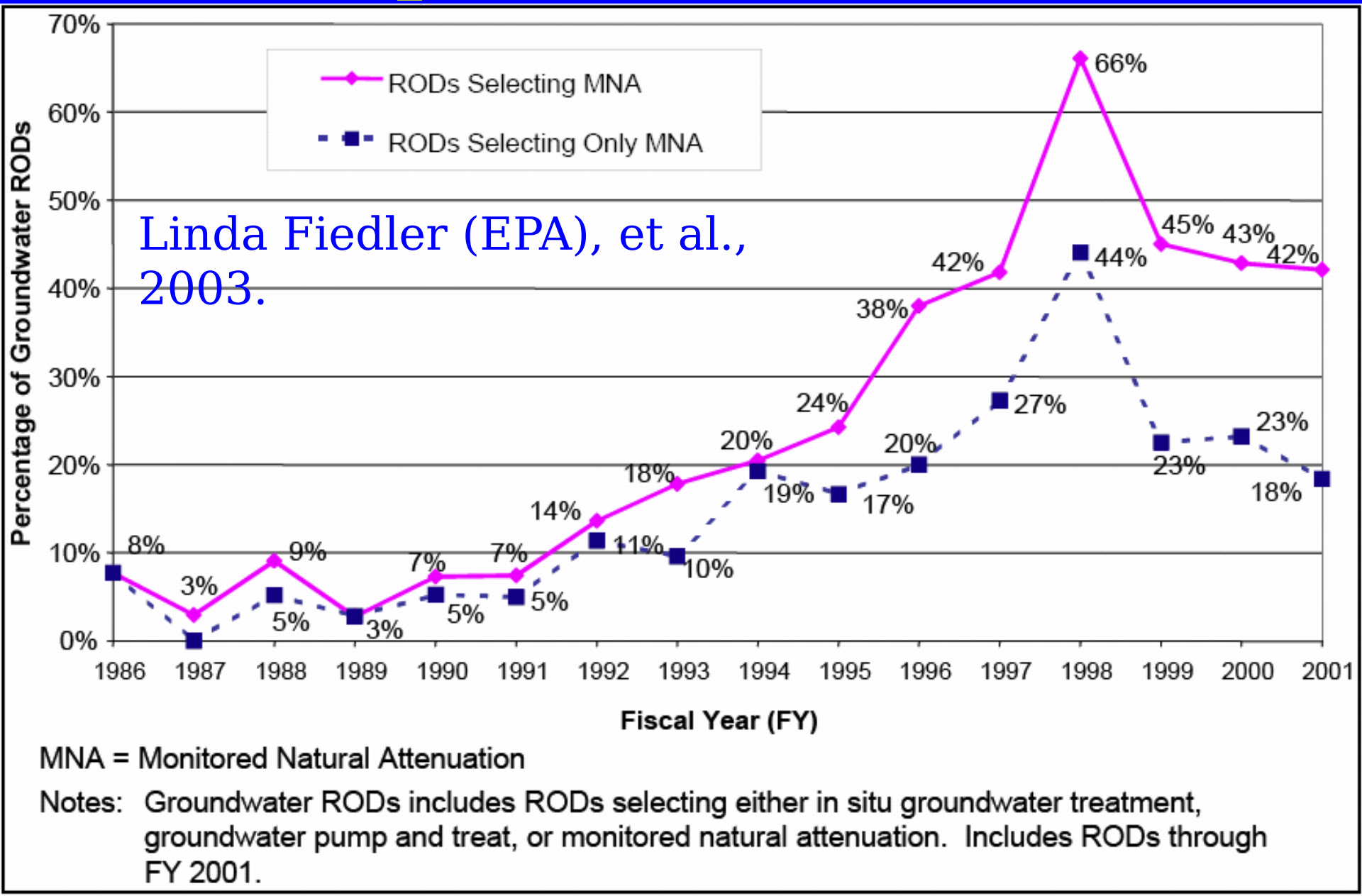
Big Picture

- Is MNA a “Faith-Based” Initiative?
  - By invoking MNA we’re putting our “faith” in natural processes
  - Entrusting the scientifically-based, natural processes w/ the responsibility to reduce contaminant concentrations
  - Must be based on good science, & the best of our historical and current knowledge of site conditions
- Trust, but Verify
  - MNA Requires either a crystal ball,
  - Or continual Verification (our responsibility)

Overview

- Importance / Definition
- Natural Processes
  - MNA Evolution
  - Contaminant Applicability
  - MNA Removal Mechanisms
- Verifying the Activity of the Natural Processes
  - Guidance
  - Data needs
  - Conceptual Model
  - Modeling tools

Importance of MNA



MNA = Monitored Natural Attenuation

Notes: Groundwater RODs includes RODs selecting either in situ groundwater treatment, groundwater pump and treat, or monitored natural attenuation. Includes RODs through FY 2001.

FIGURE 7. Superfund MNA remedies selected.

Definition of MNA

1999 MNA directive from EPA's Office of Solid Waste and Emergency Response (OSWER) :

The term "natural attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants.

Definition of MNA

Moreover, part of the context for this review is the public concern about possible misapplication of natural attenuation. Some view this technique as a "do nothing" approach. For example, a feature article (*Environmental Science & Technology*, Volume 34, Issue 15, August 1, 2000, pages 346-353) quotes a prominent environmental scientist as saying that natural attenuation is a,"low-cost, ineffective approach that delays the inevitable need to clean up the site." Clearly, some

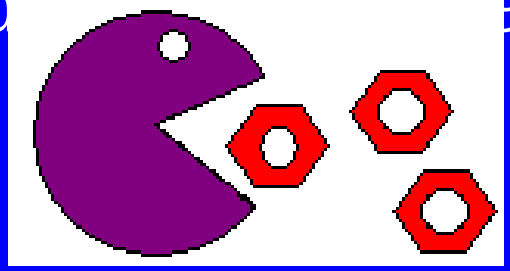
EPA Definition

- Monitored Natural Attenuation (MNA):

. . . the use of ***natural attenuation processes*** *within the context of a carefully controlled and monitored site cleanup approach that will reduce contaminant concentrations to levels that are protective of human health and the environment within a* ***reasonable time frame***.

MNA Evolution

- 1991- Where's the Benzene? Examining California ground-water quality surveys: Groundwater vol 29.



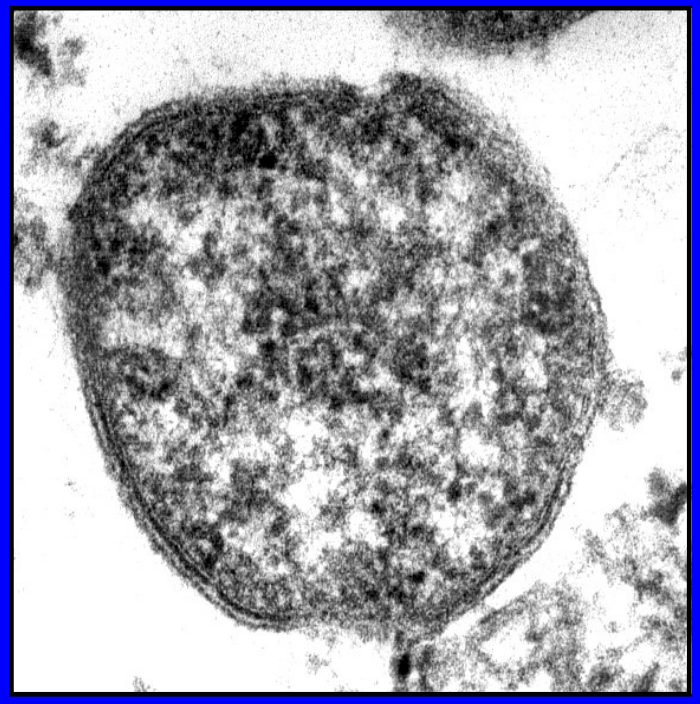
- 1995 - "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTS)," Lawrence Livermore National Laboratory.

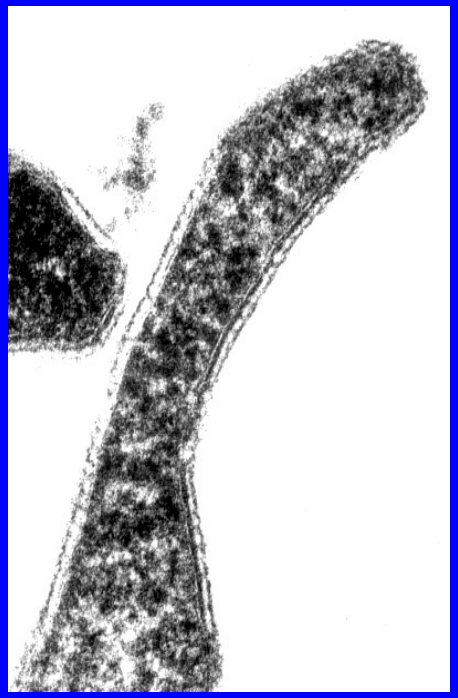
MNA Evolution

- 1993 – “Halorespiration”
  - Reduction of PCE to DCE coupled to growth
- 1995 – *Dehalococcus ethenogenes*
  - strain 195
  - Dechlorination of PCE to VC and ethene.

Dehalococcus ethenogenes

Thin-section electron micrographs showing coccoid and elongated cells



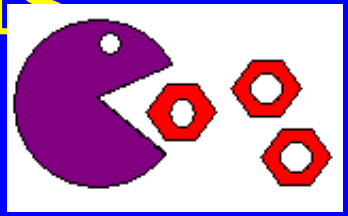


Photos courtesy of Dr. Steve Zinder, Cornell Univers

Contaminant Applicability

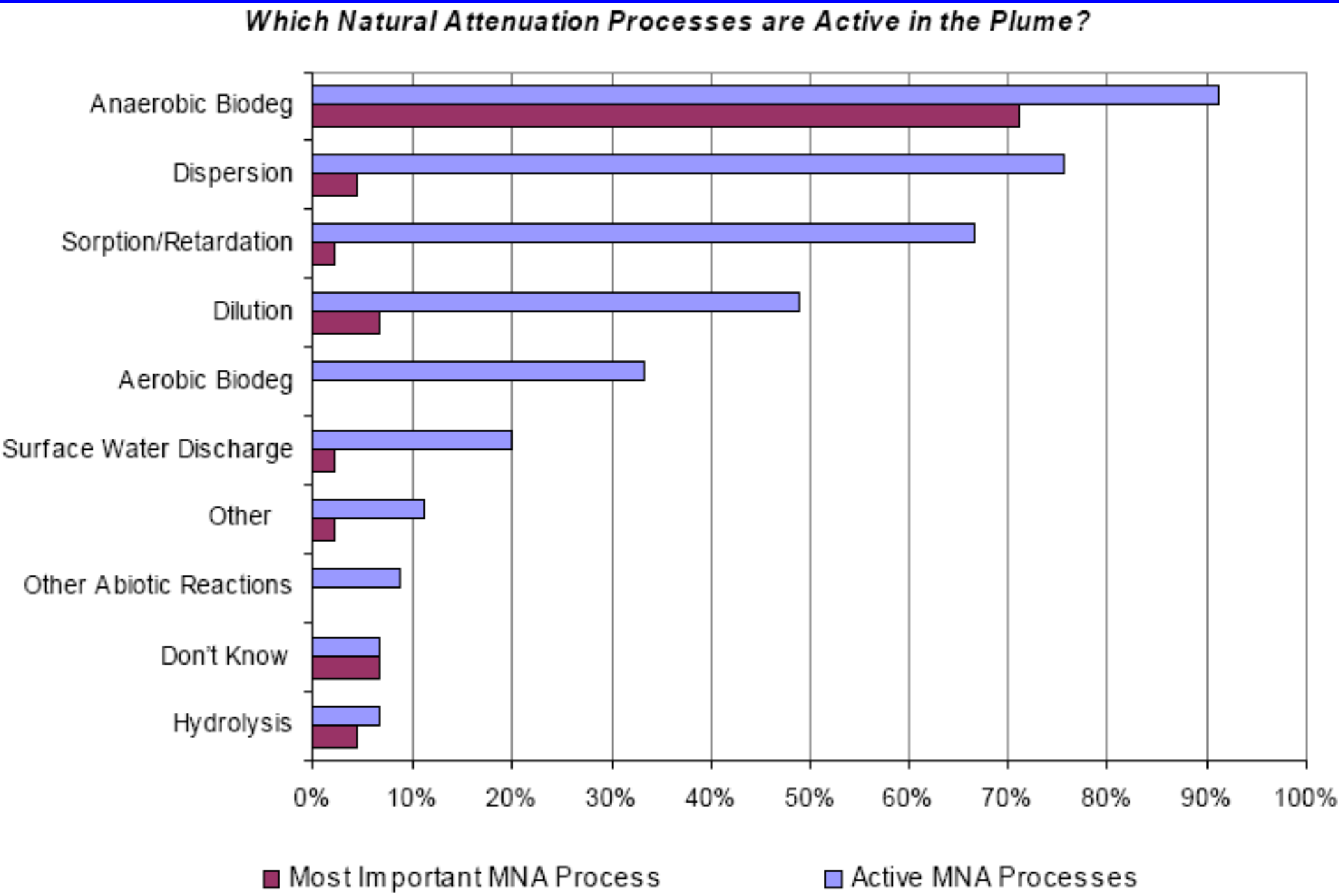
- Fuel Hydrocarbons - Well Established
- Chlorinated Organics - a Possibility Under the Right Circumstances
- Explosives - Army Now Exploring Applicability (Again,likely Only Under Specific Conditions)
- Metals - Geochemical Question

MNA Removal Mechanisms



- Biodegradation
- Chemical reactions (abiotic)
  - Fe-bearing soil Minerals (e.g., magnetite)
  - Hydrolysis (usually very slow)
- Dilution and dispersion
- Sorption
- Evaporation

MNA Removal Mechanisms



MNA Removal Mechanisms

Biodegradation

- Microbiology Overview
  - Electron Donors
  - Electron Acceptors
  - Contaminants as E-donors / E-acceptors
- Biodegradation Processes for CVOCs
  - Reductive Dechlorination
  - CVOC as Electron Donor
  - Cometabolism

MNA Removal Mechanisms

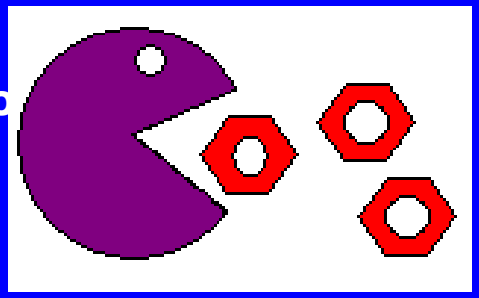
Biodegradation / Microbiology Overview

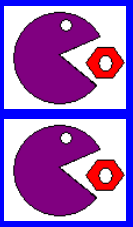
Humans

- **Carbon source: Food**
- **Energy source (e-donor): Food**
- **Respiration (e-acceptor): Oxygen**

Bacteria

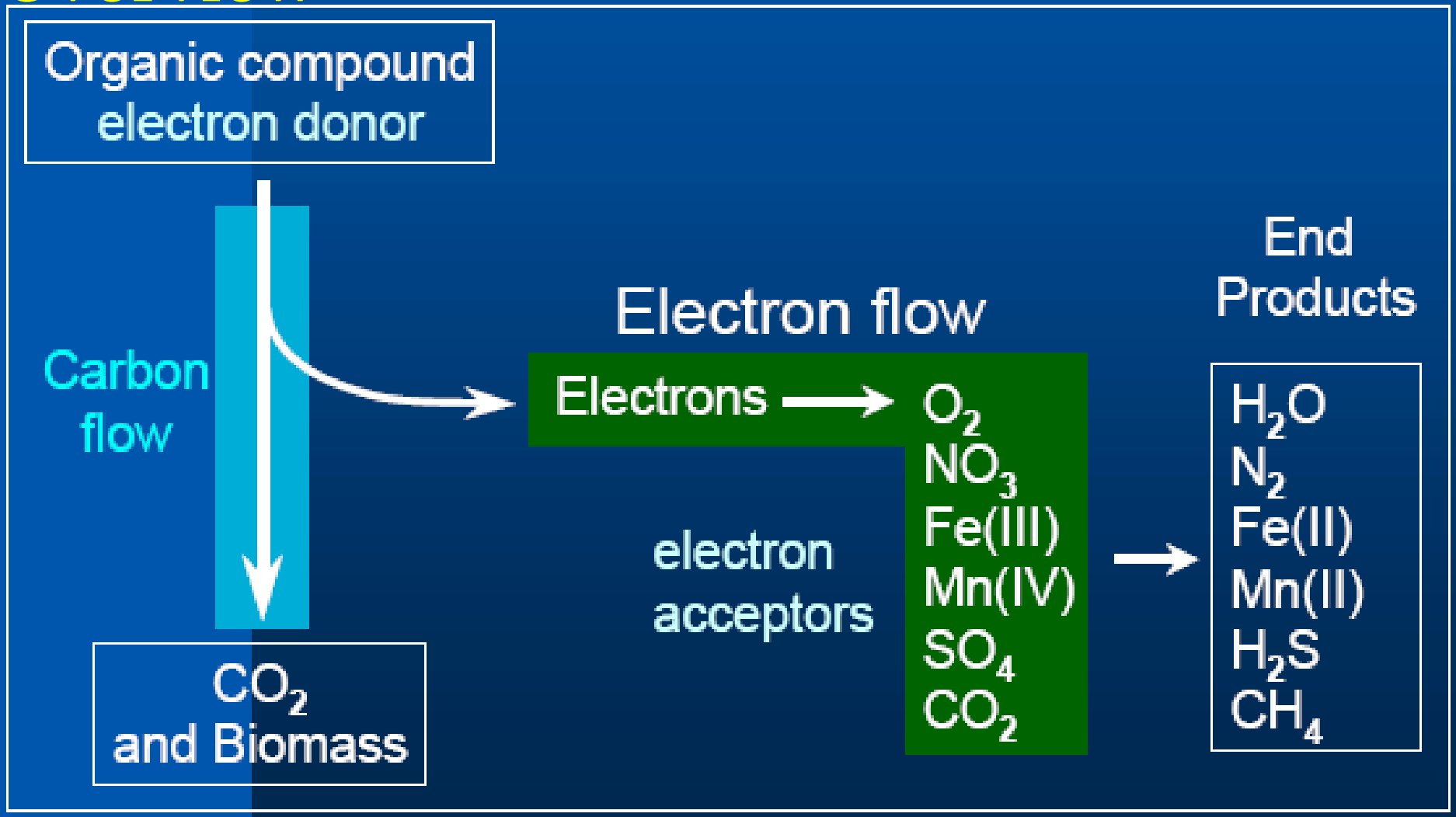
- **Carbon source: Organic Carbon**
- **Energy source (e-donor): Organic Carbo**
- **Respiration (e-acceptor):**
  - **Aerobes: Oxygen**
  - **Anaerobic: NO3, Fe III, SO4, CO2**





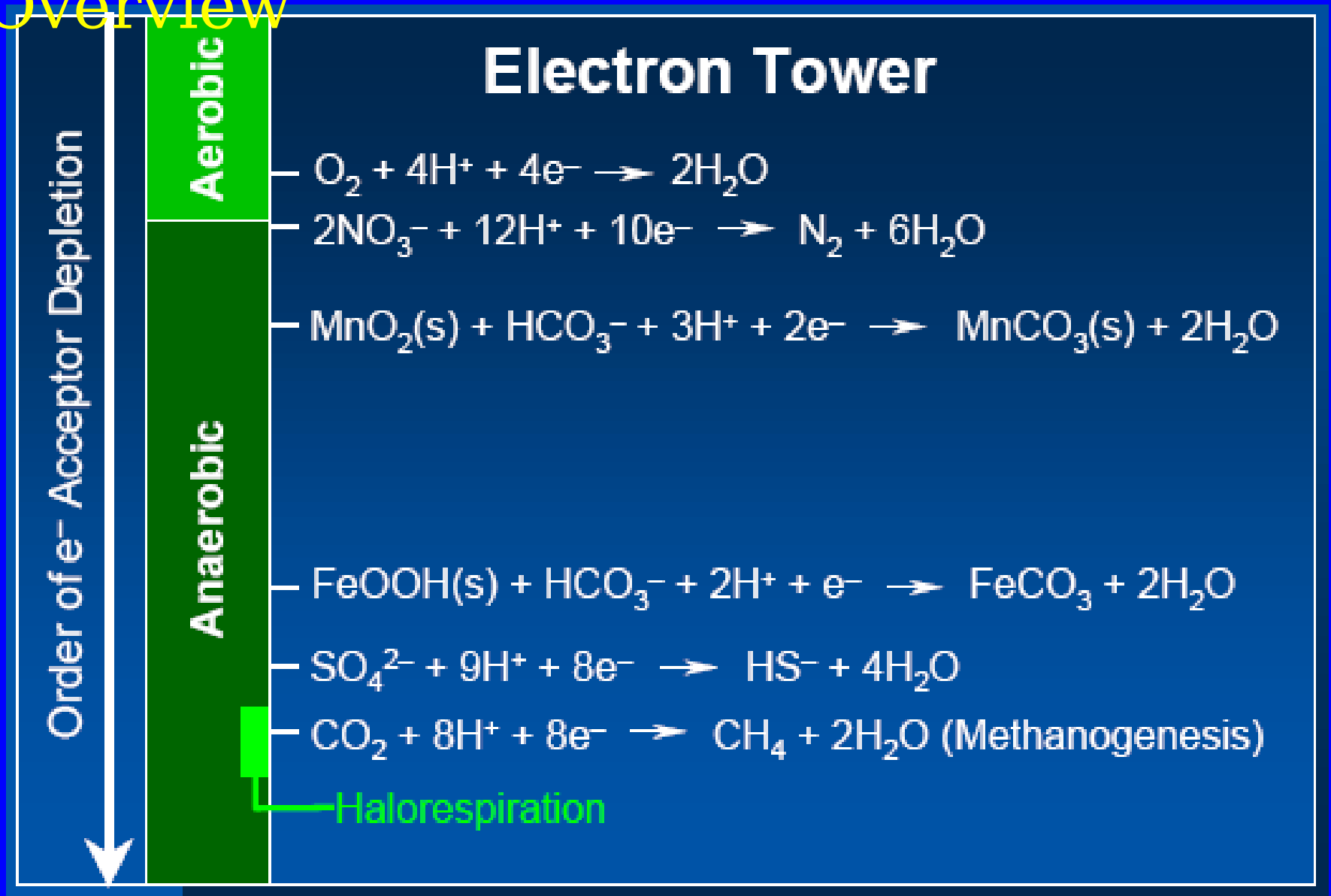
MNA Removal Mechanisms

Biodegradation / Microbiology Overview



MNA Removal Mechanisms

Biodegradation / Microbiology Overview


Electron Tower
Order of e⁻ Acceptor Depletion
Aerobic
Anaerobic
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$
$MnO_2(s) + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_3(s) + 2H_2O$
$FeOOH(s) + HCO_3^- + 2H^+ + e^- \rightarrow FeCO_3 + 2H_2O$
$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ (Methanogenesis)
Halorespiration

MNA Removal Mechanisms

Biodegradation Processes for CVOCs

- Reductive Dechlorination: CVOC can be dechlorinated under strict anaerobic conditions.
- CVOC serves as Electron Donor: CVOC used as carbon and energy source under aerobic or mildly reducing conditions (only applicable to 2 chloroethenes, VC & possibly DCE?) .
- Cometabolism: CVOC fortuitously dechlorinated by enzymes made to the degrade a primary substrate.

MNA Removal Mechanisms

Biodegradation Processes for CVOCs -Reductive Dechlorination

- Respiratory process: Halorespiration
  - e– donor: Lactate
  - e– acceptor: Chloroethenes
- Lactate fermentation:

  Lactate → Acetic Acid

  $C_3H_6O_3 + H_2O \rightarrow CH_3COOH + CO_2 + 2H_2$
- PCE dechlorination to ethene:

  PCE → Ethene

  $C_2Cl_4 + 4H_2 \rightarrow C_2H_4 + 4HCl$
- $PCE + 2Lactate + 2H_2O \rightarrow Ethene + 2Acetic\ Acid + 2CO_2 + 4HCl$

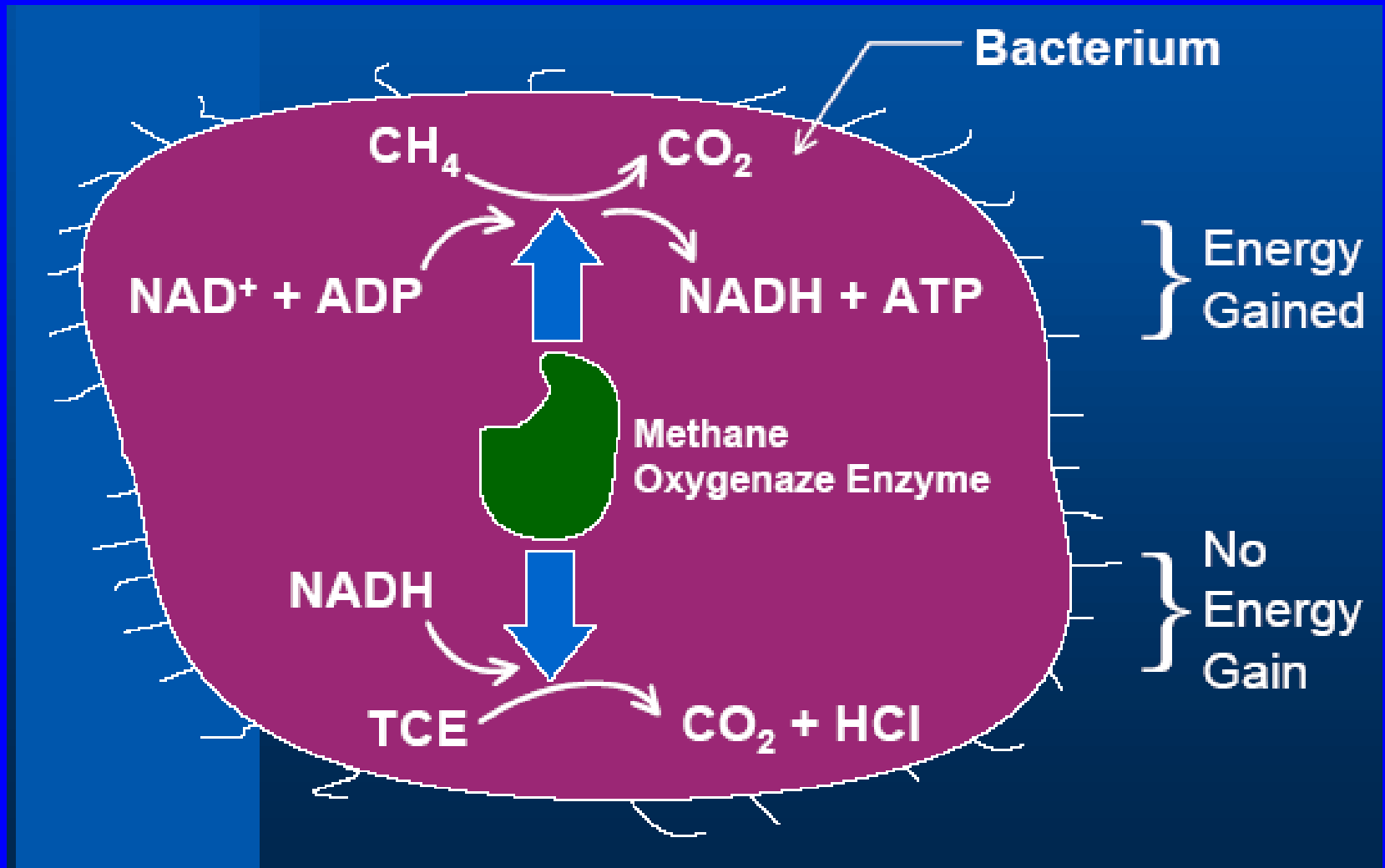
MNA Removal Mechanisms

Biodegradation Processes for CVOCs - CVOC serves as Electron Donor

- Bacteria use CVOC for Carbon & Energy
- Only applicable to 2 chloroethenes
  - VC & possibly DCE
- Electron Acceptors
  - Aerobic: O2,
  - Anaerobic: NO3, Mn IV, Fe III

MNA Removal Mechanisms

Biodegradation Processes for CVOCs -Cometabolism



MNA Removal Mechanisms

Biodegradation Processes for CVOCs

- Summary of Biodegradation Mechanisms
  - Reductive Dechlorination: CAHs can be dechlorinated under strict anaerobic conditions
  - CAH as a growth substrate: CAHs are used for carbon and energy (chloroethenes restricted to VC and DCE) under aerobic or mildly reduced conditions
  - Cometabolism: CAHs destroyed fortuitously by enzymes made to degrade a primary growth substrate

MNA Removal Mechanisms

- MNA is complex
  - Many things happening at once
  - Some mechanisms poorly understood
- Determining the extent to which MNA is occurring is Challenging.
- MNA requires a Multi-Disciplinary effort
  - MNA Team: Geologists, Chemists, Engineers, & Environmental Scientists must collaborate to develop characterization & monitoring plans.

Verifying the Activity of the Natural Processes

- Guidance
- Data needs
- Conceptual Model
- Modeling tools

Guidance

- AFCEE Protocols for Fuel Hydrocarbons, Chlorinated Organics
- Navy Technical Guidelines
- EPA OSWER Policy Directive 9200.4-7
- ERDC (formerly WES) Reports on Natural Fate of Explosives

Guidance

- 1995 Memorandum: Interim Army Policy on Natural Attenuation for Environmental Restoration
  - Requires consideration of natural attenuation as a remedial action alternative for all restoration decisions.
  - An engineered remedial action will not be approved unless data exists to prove that natural attenuation is inappropriate for a site cleanup.

Guidance

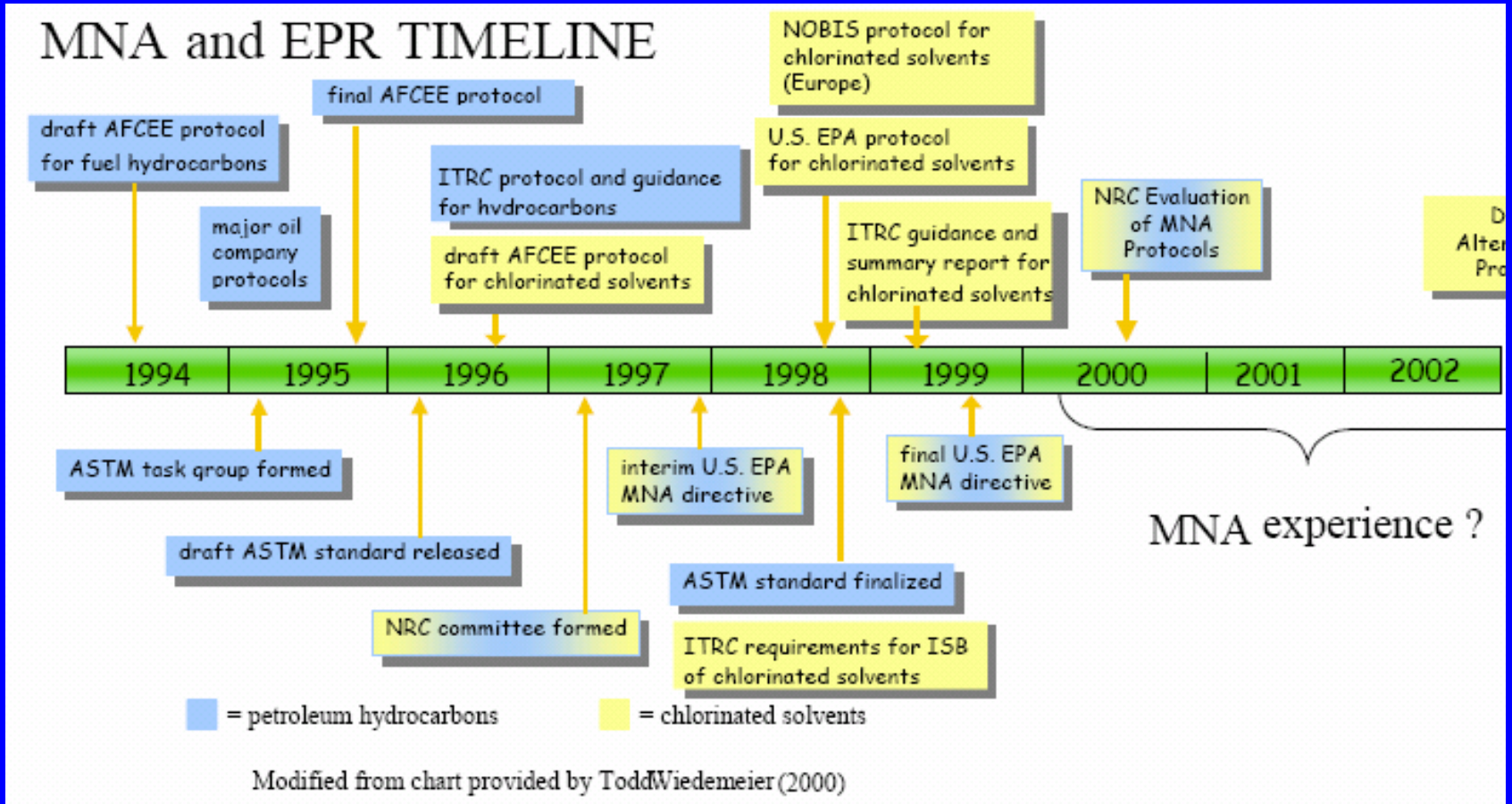
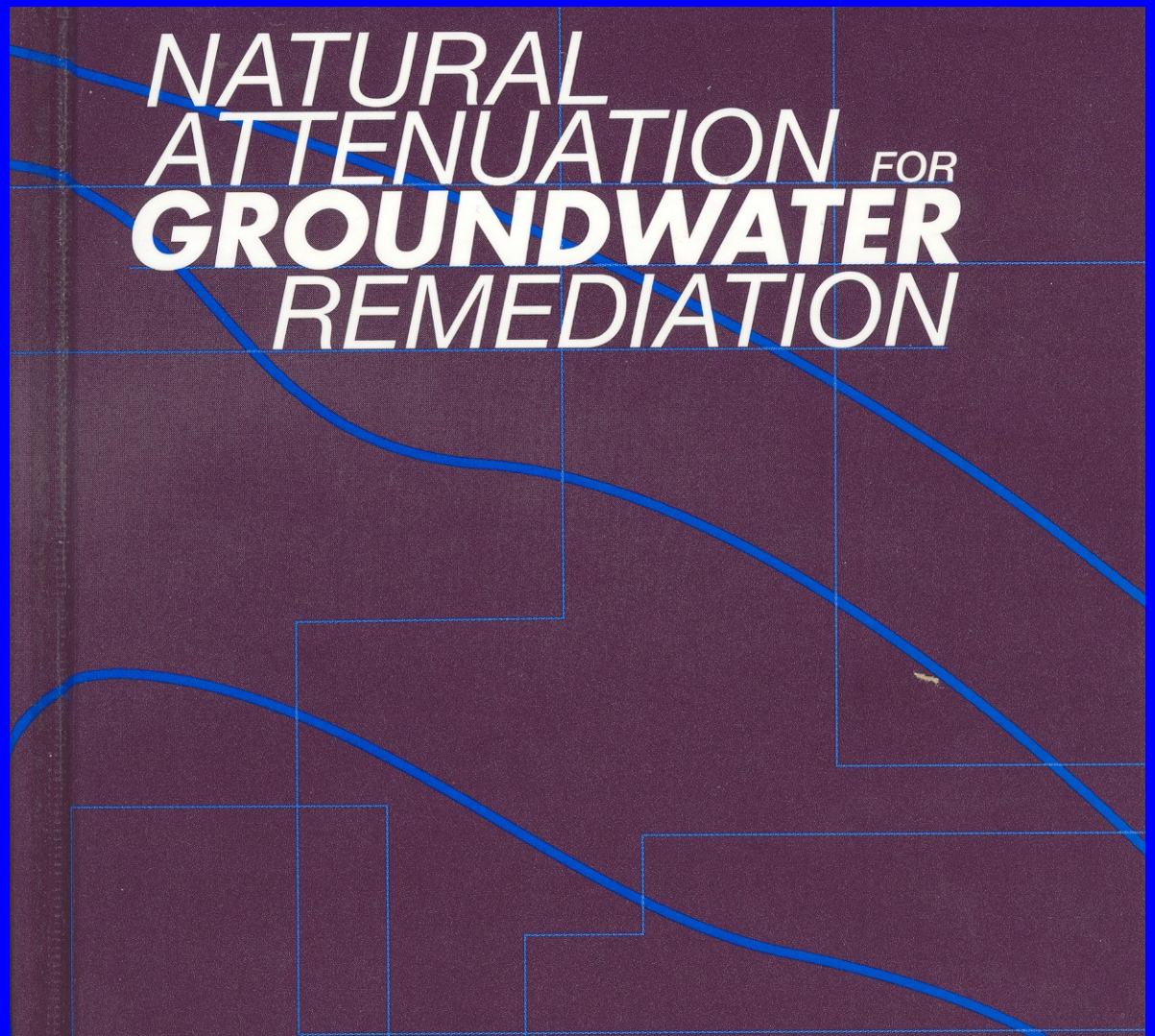


FIGURE 3. Recent Historical Development of MNA/EPR for Petroleum Hydrocarbons and Chlorinated Solvents (Wiedemeier and Barden, 2002)

Guidance



Guidance

NRC Findings

- Level of Effort to show MNA depends on:
  - Type Contaminant(s)
  - Site Complexity
- Focus on Conceptual Site Model, Geochemical Footprint, & Monitoring
  - De-emphasize AFCEE site scoring system
- Re-emphasizes need for proper characterization
  - Especially regarding hydrogeology

MNA Data Needs

- Three Lines of Evidence may be required to demonstrate efficacy of MNA
  - 1. Historical Data Demonstrates Declining Contaminant Concentrations
  - 2. Hydrogeologic and Geochemical Data Indicating NA Processes and Rates
  - 3. Field or Lab Microcosm Studies (Unnecessary at many Sites)
- Unless #1 is of sufficient quality & duration, #2 is generally required (regulatory decision).

MNA Data Needs

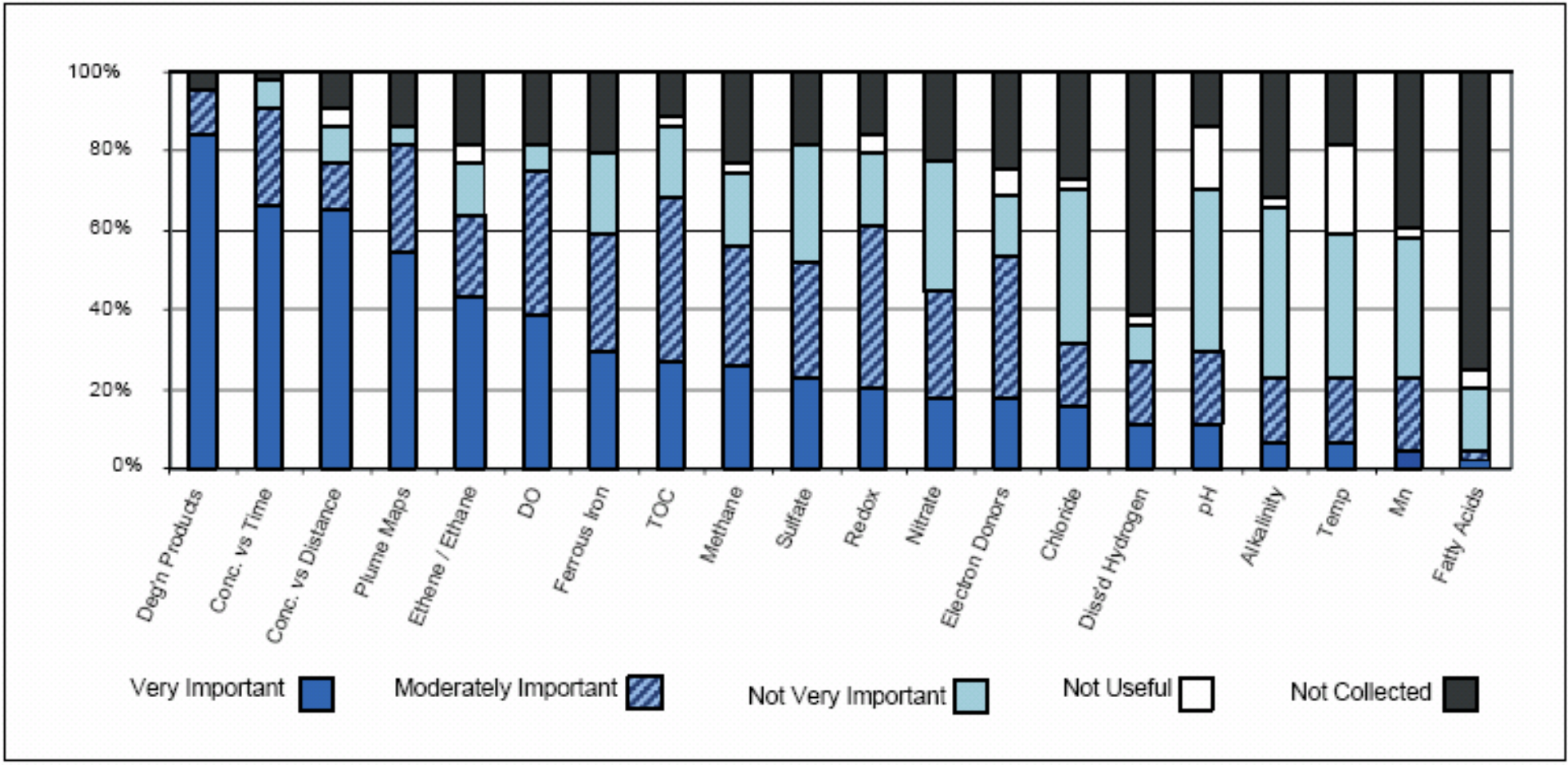
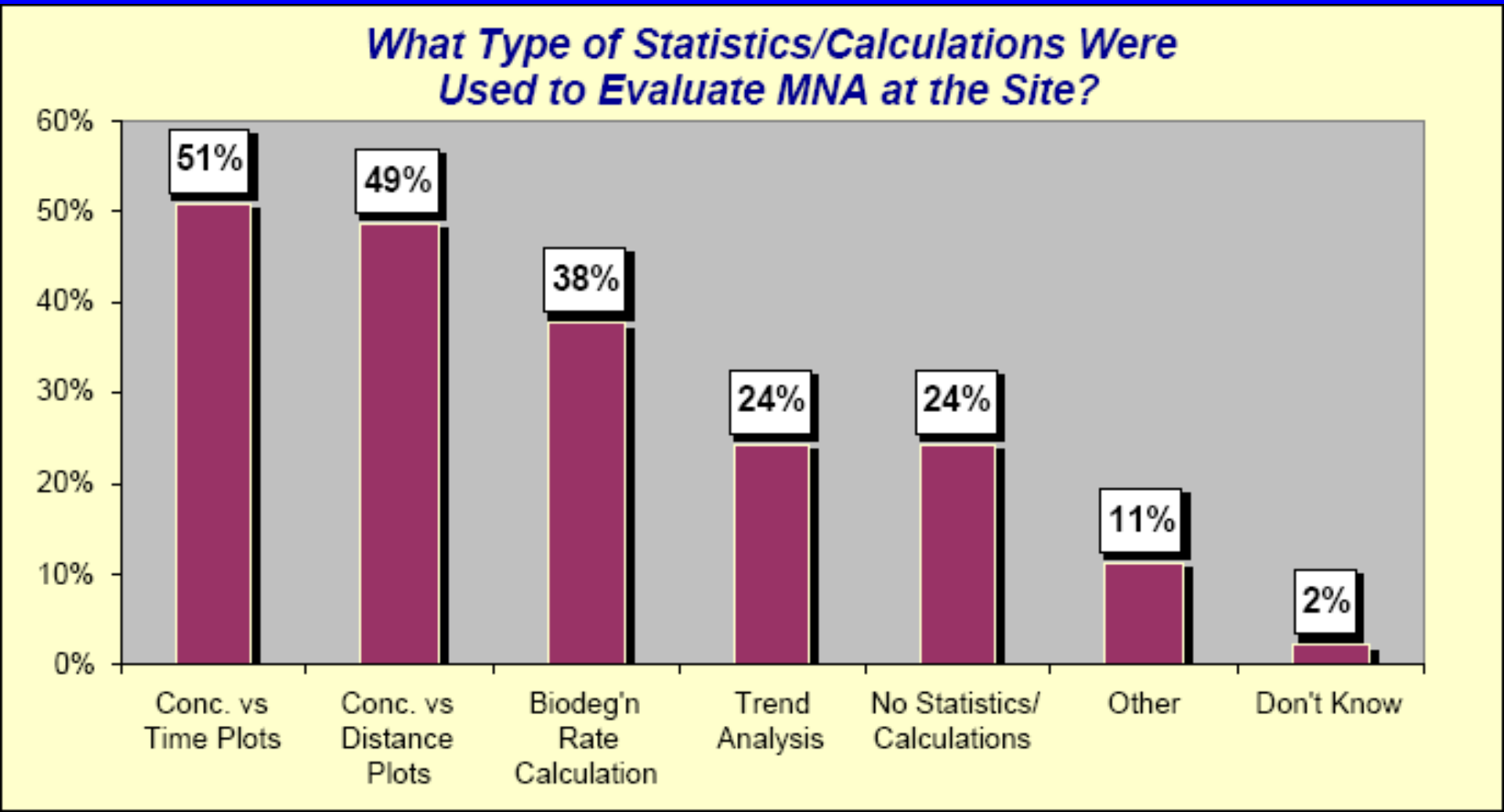


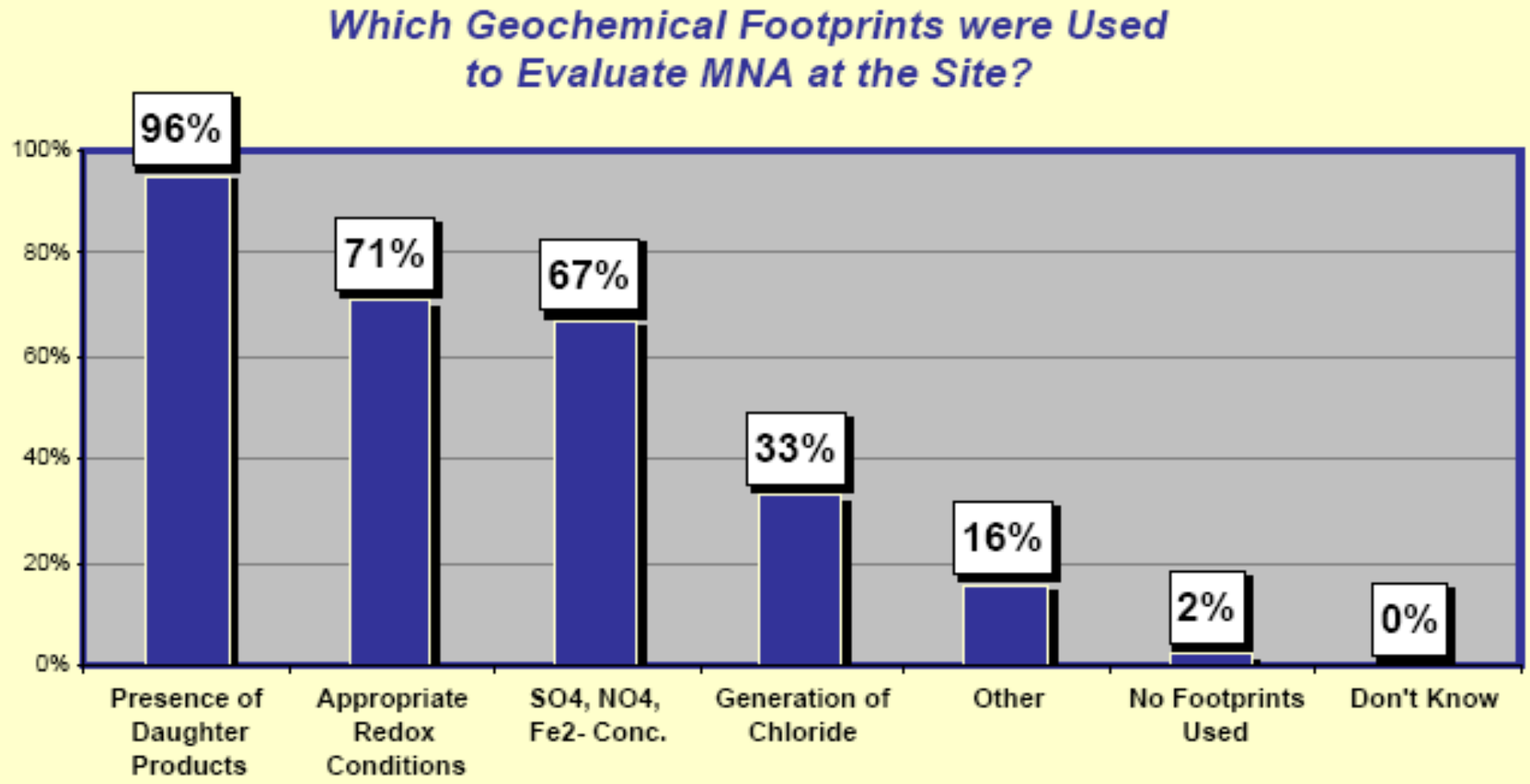
FIGURE 1. Field data collected to evaluate MNA and relative importance

Emerging molecular biology methods – RNA / DNA probes

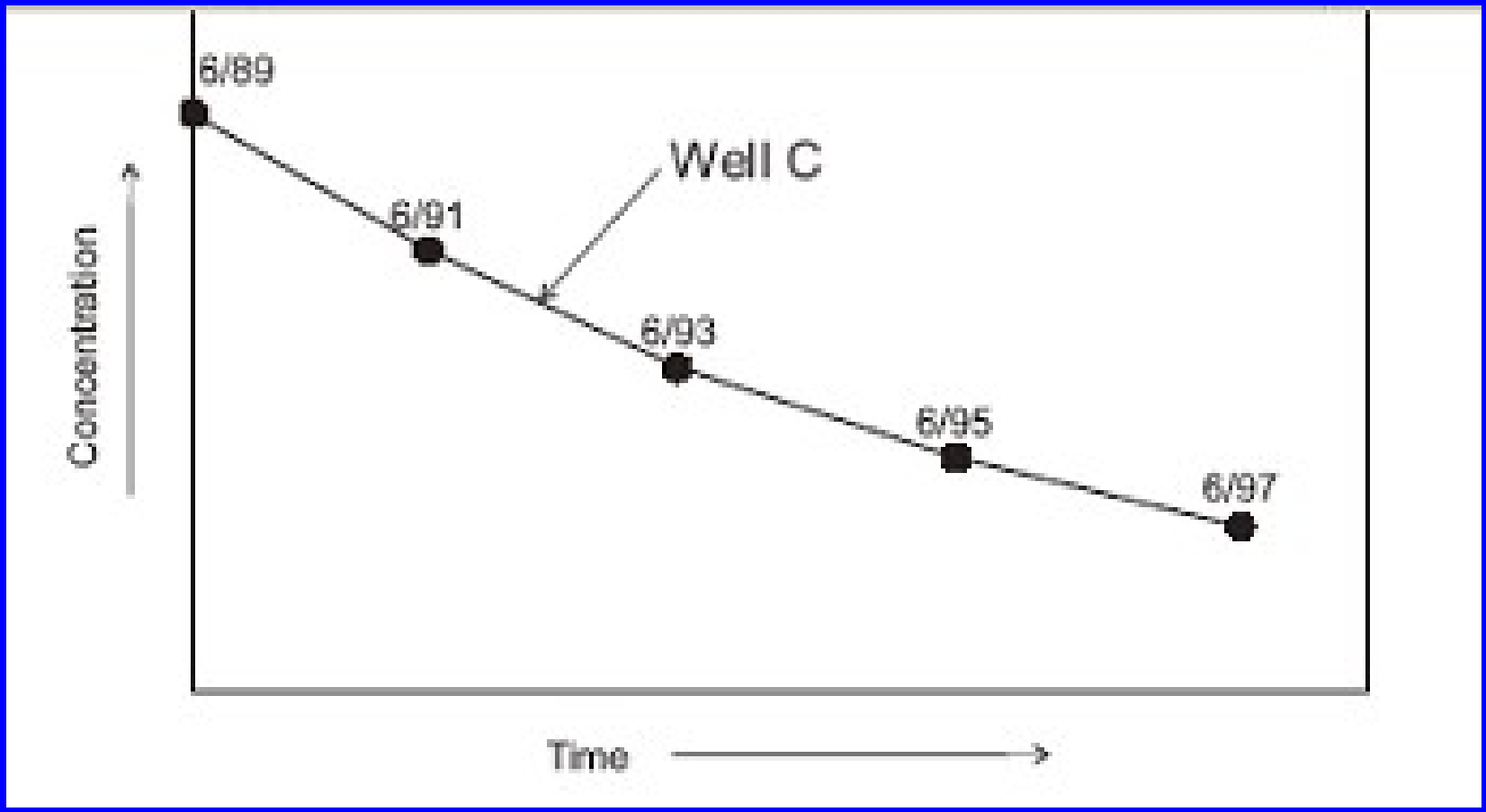
MNA Data Needs



MNA Data Needs



MNA Data Needs



Concentration vs. Time Attenuation Rate Constant, where a rate constant, in units of inverse time (e.g., per day), is derived as the slope of the natural log concentration vs. time curve measured at a selected monitoring location (Figure 1).

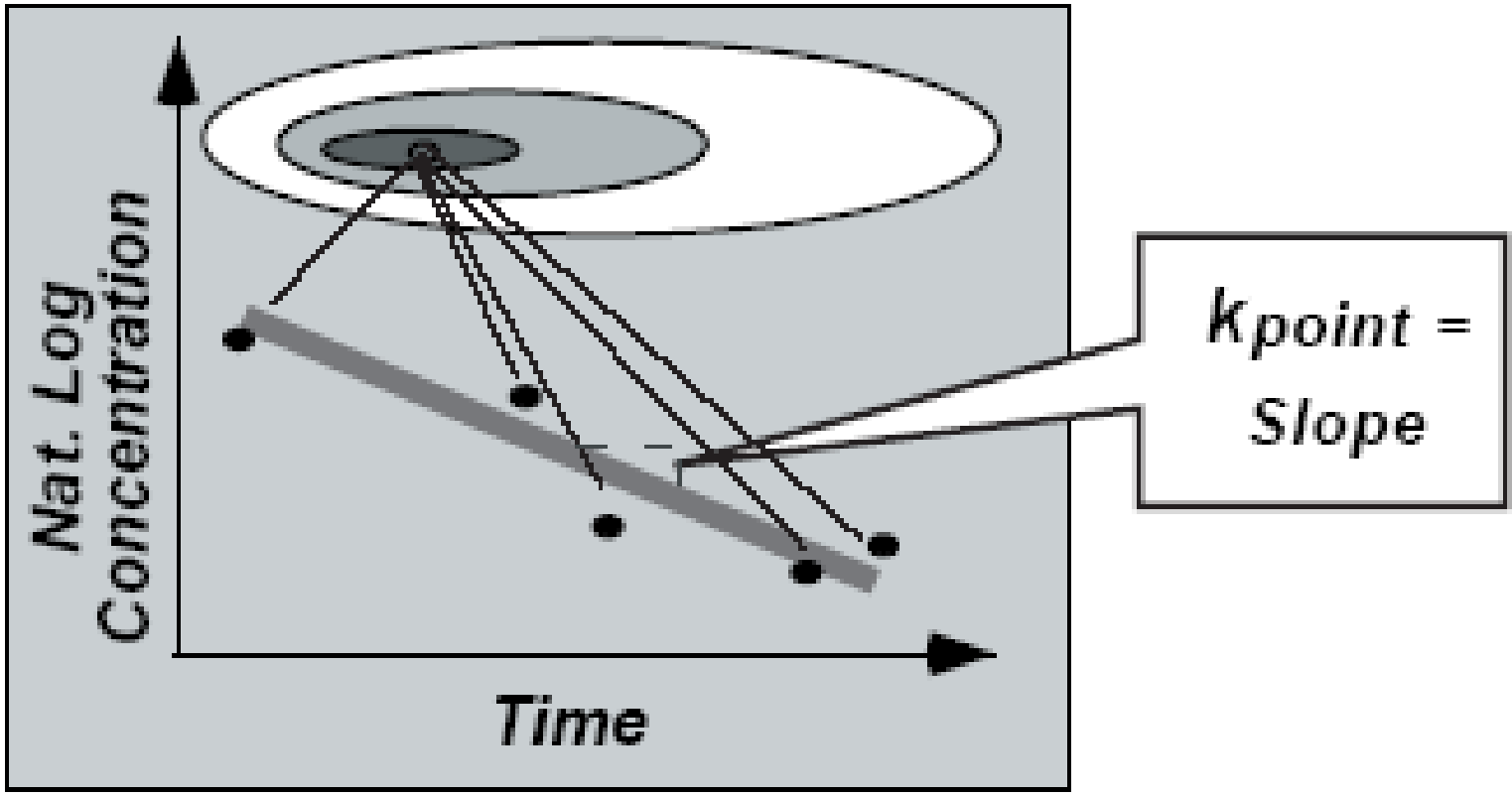
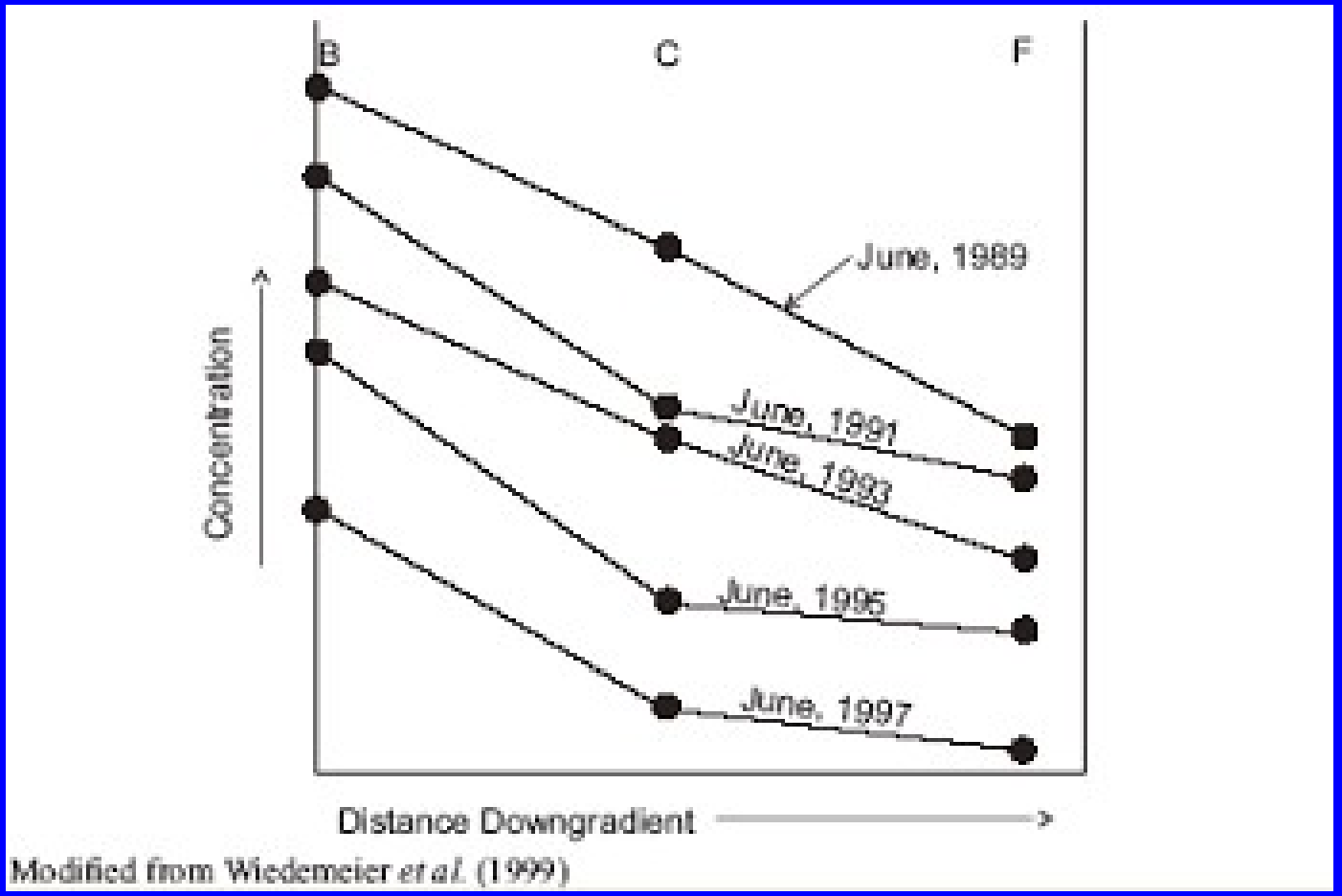


Figure 1. Determining concentration vs. time rate constant (k_{point}).

MNA Data Needs



Modified from Wiedemeier *et al.* (1999)

Concentration vs. Distance Attenuation Rate Constant, where a rate constant, in units of inverse time (e.g., per day), is derived by plotting the natural log of the concentration vs. distance and (if determined to match a first-order pattern) calculating the rate as the product of the slope of the transformed data plot and the ground-water seepage velocity (Figure 2).

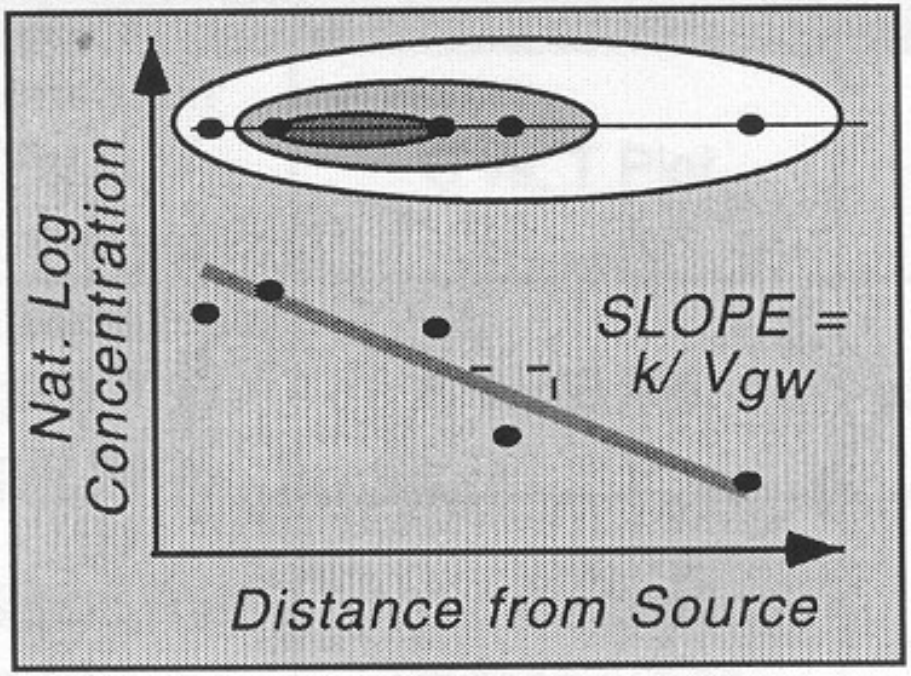


Figure 2. Determining concentration vs. distance rate constant (*k*).

EPA
United States
Environmental Protection
Agency

Ground Water Issue

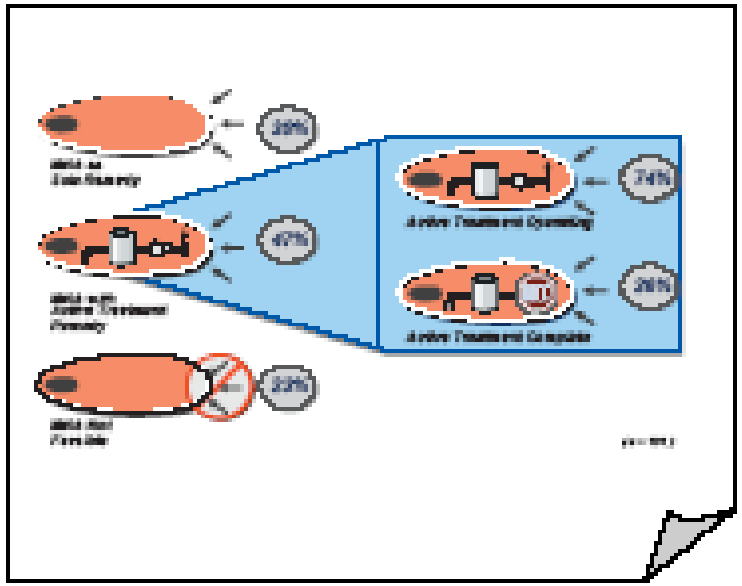
Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

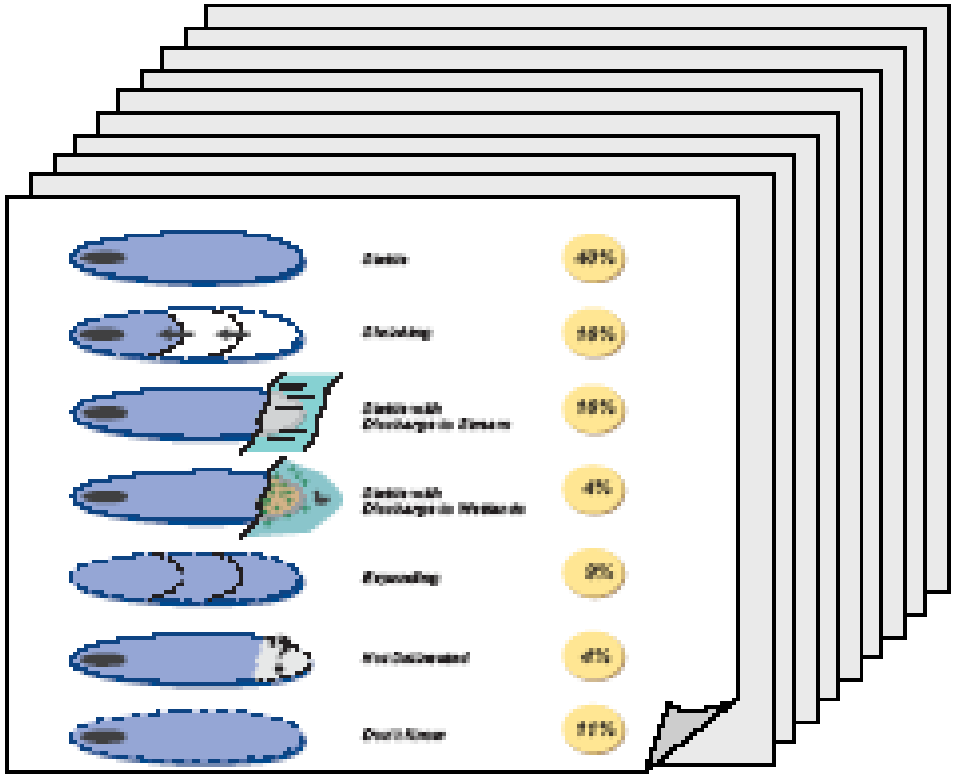
Charles J. Newell[1], Hanadi S. Rifai[2], John T. Wilson[3], John A. Connor[1], Julia A. Aziz[1], and Monica P. Suarez[2]

- Conservative Assumptions should be used when Estimating Future Trends.

Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents

November 1, 2003





MNA Data Needs

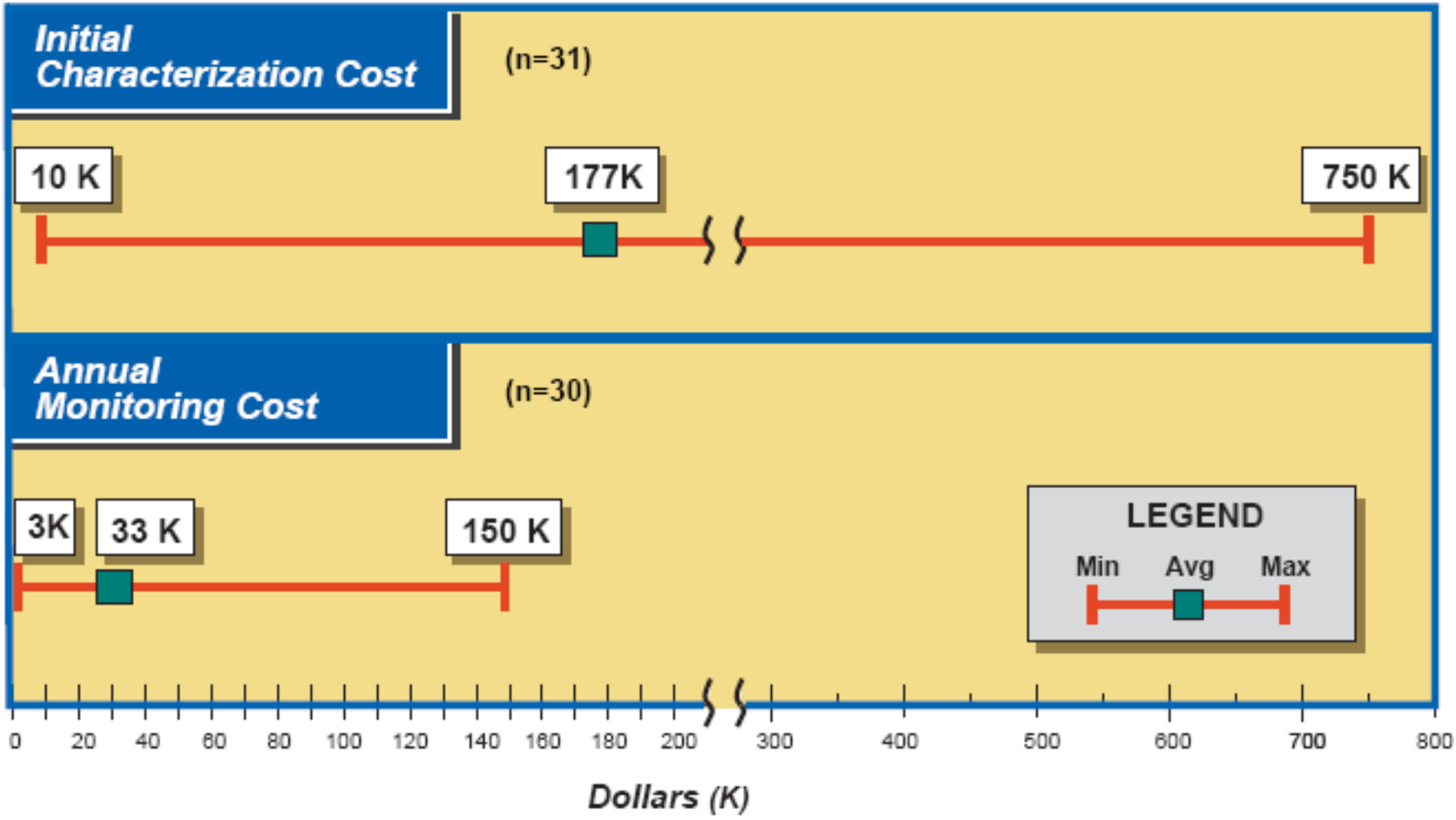


Figure 5.4
Typical Costs Associated with MNA

MNA Data Needs

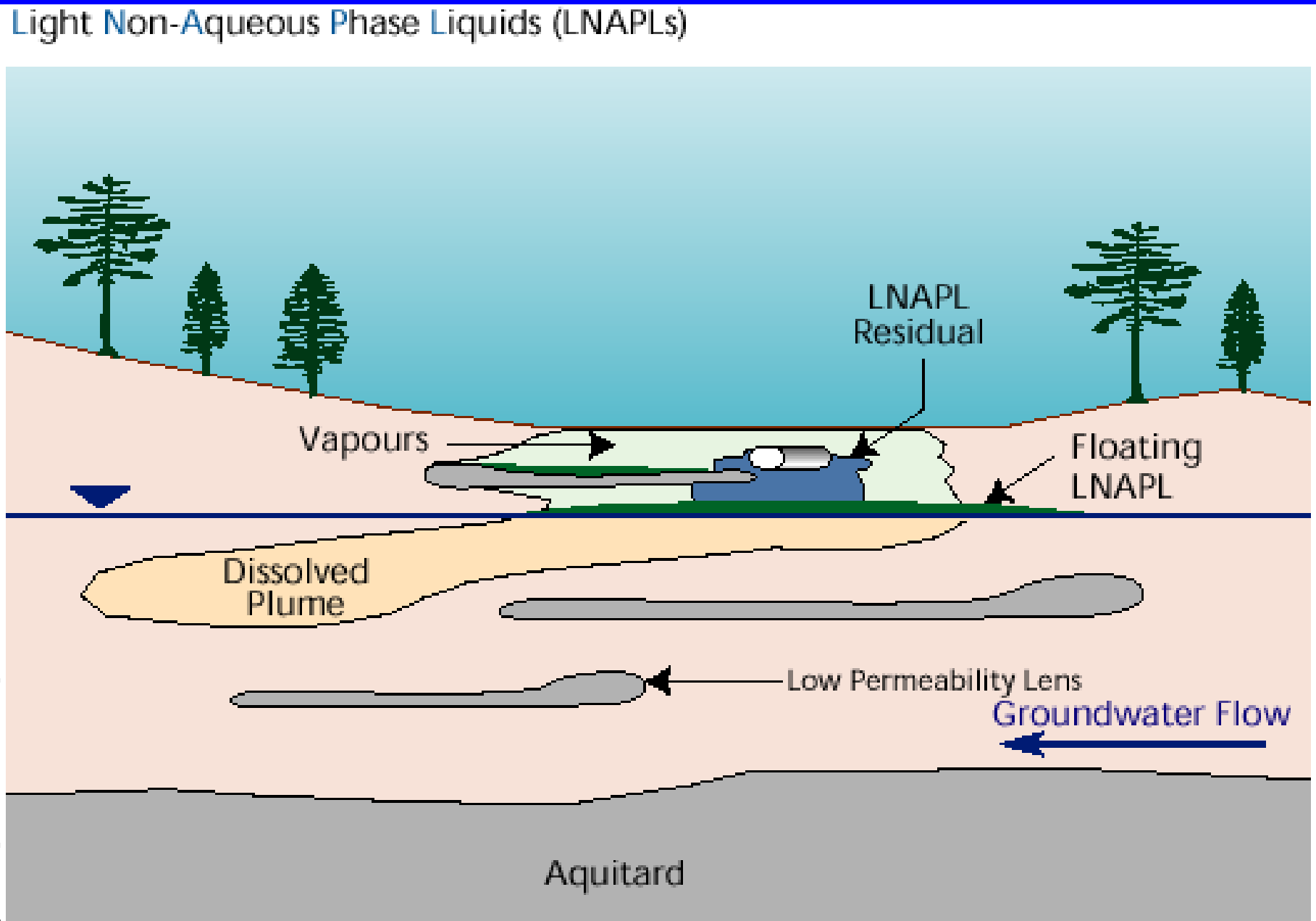
Emerging Data Needs - Wish List

- Mineralogical Testing
  - Magnetite
  - FeS, FeS2
- Molecular Biology Tools
  - Nucleic Acid Probes
    - DNA - presence / absence
    - mRNA - activity (real-time PCR)
  - Enzyme Assays

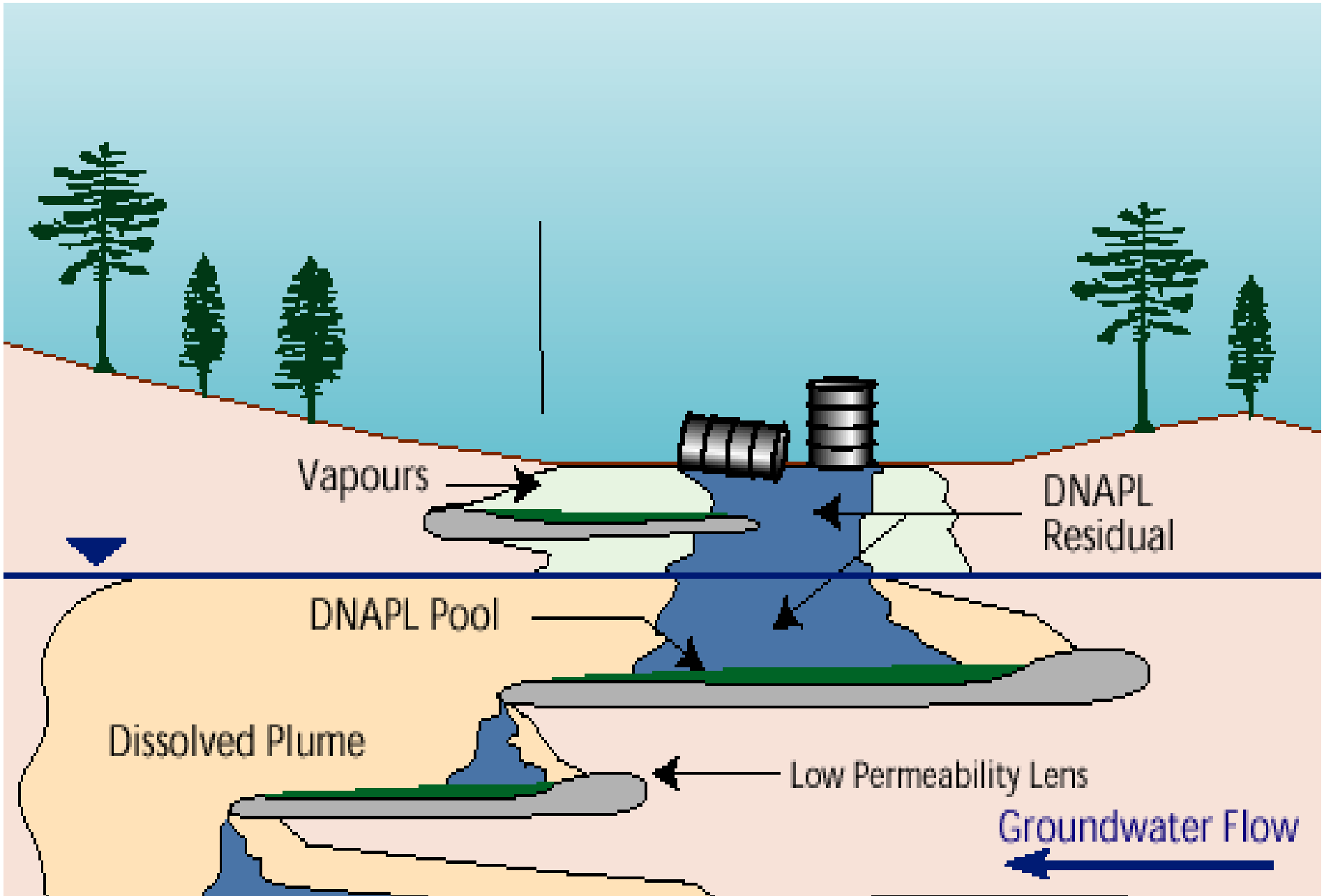
Conceptual Site Model (CSM)

Attempt to visualize the distribution of contaminants on a site

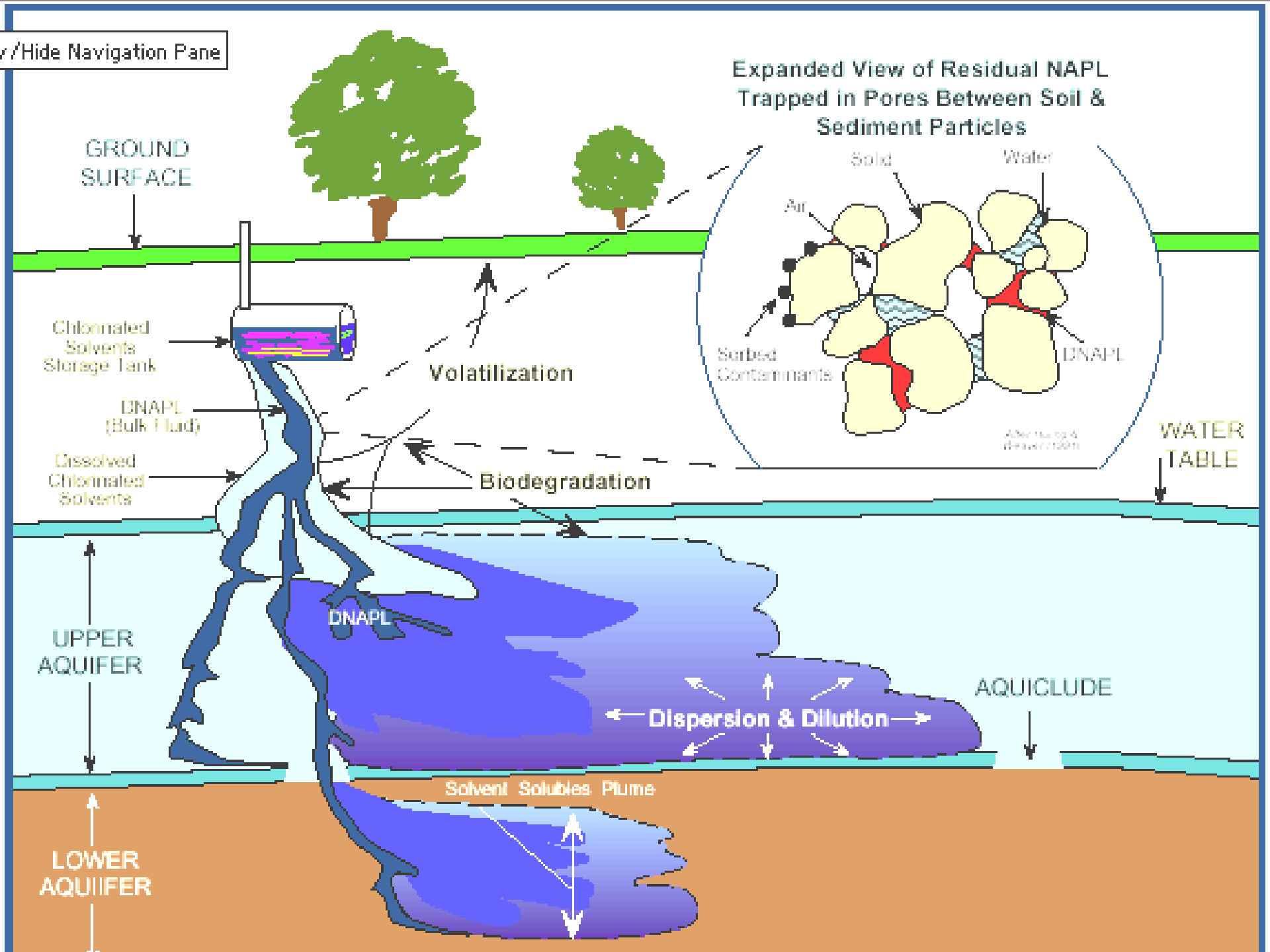
Conceptual Site Model



Dense Non-Aqueous Phase Liquids (DNAPLs)



v/Hide Navigation Pane



Conceptual Site Model

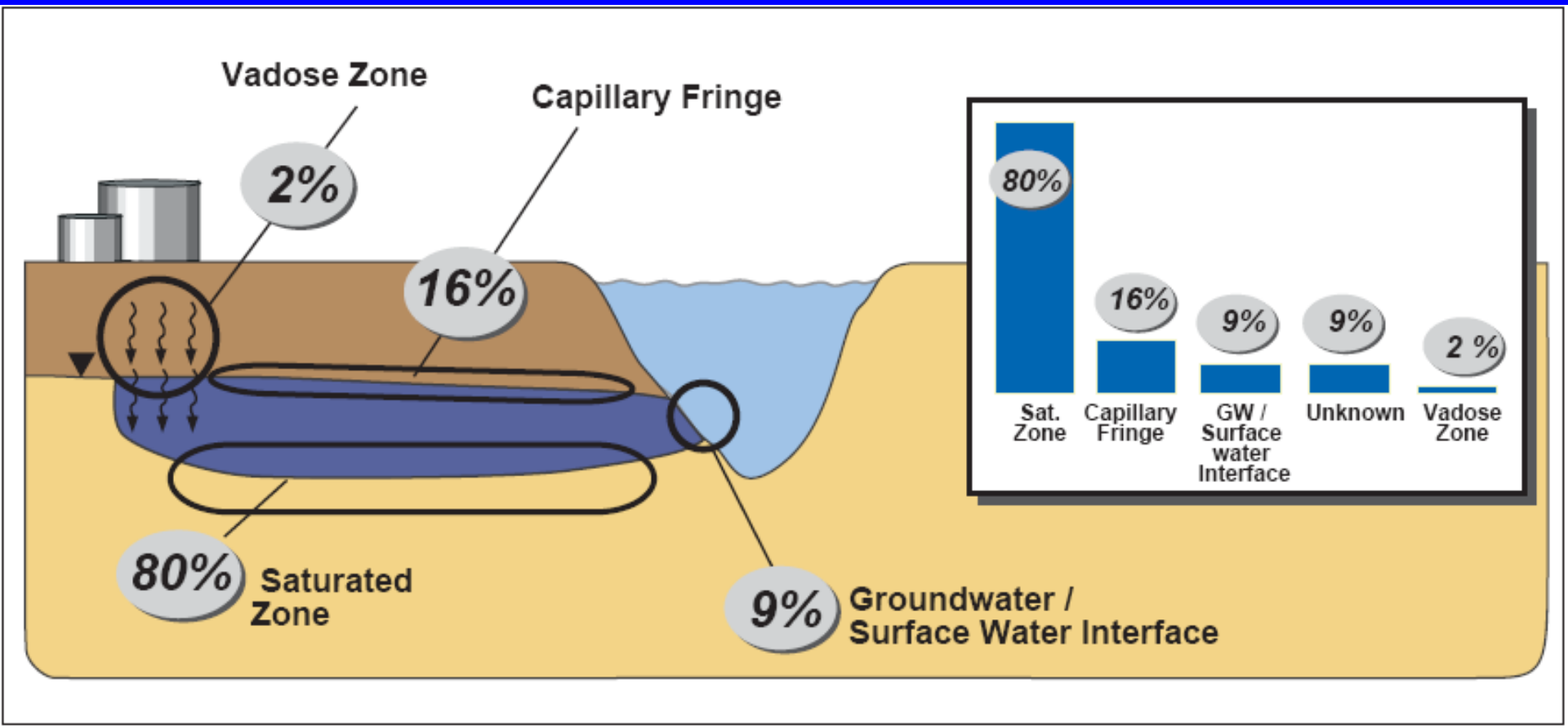


Figure 5.11
Primary Subsurface Location of Attenuation Processes (n=45)

Conceptual Site Model

- Conceptual Site Models should be continuously updated to fit monitoring data.

Modeling Tools

- Models (Can Be Used for Active Bioremediation, Too)
- Bioscreen & Biochlor
  http://www.epa.gov/ada/csmos/models.html
  - Excel-based, Biochlor 2.2 allows constant or decaying source term
- MAROS http://www.gsi-net.com/software/Maros.htm
  - MNA trend analysis / statistics
- SOURCE DK http://www.gsi-net.com/Software/SourceDK.htm
  - To estimate remediation time-frames when NAPL is present
- NAS http://ceeweb.cee.vt.edu/nas/index.html
  - Must estimate NAPL mass in source zone
  - Time of Remediation vs, full or partial NAPL removal
- Mass Flux Toolkit - hasn't been released yet
  - Mass flux from source areas, for MNA evaluations, etc

Conclusions

- Like a Site Conceptual Model, our knowledge of MNA is continually evolving.
  - Discovery of previously unrecognized removal mechanisms continues to occur.
- New analytical techniques continue to be developed (e.g, DNA / RNA probes).
- New modeling tools have been developed that were not previously available.

Conclusions

- Determining the extent to which MNA is occurring represents a Substantial Challenge.
- The level-of-effort for MNA will be driven by type of Contaminant & Site Complexity.
- MNA requires a Multi-Disciplinary effort; Geologists, Chemists, Engrs, & Environ Scientists must collaborate to ensure adequate characterization & monitoring.